LARGE AMPLITUDE MOTIONS AND π-HYDROGEN BONDING IN THE THIOPHENE–WATER COMPLEX CHARACTERIZED BY ROTATIONAL SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

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The rotational spectrum of the thiophene–water (thiophene–w) complex was studied for the first-time using Fourier transform microwave (FTMW) spectroscopy from 7 to 20 GHz. Supported by density functional theory (DFT) calculations, transitions belonging to a single dominant conformer were observed in the spectrum. By comparing the experimentally derived spectroscopic parameters, which includes data for the singly substituted ^{18}O isotopic species, with the results from quantum chemical calculations at the B2PLYP-D3(BJ)/def2-TZVP level of theory, we show that the observed pattern of transitions is consistent with a structure that is highly averaged over a large amplitude rocking motion of the water. This effective geometry, stabilized via a primary O–H...π hydrogen bond, has the oxygen atom of water sitting above the plane of the thiophene molecule centered on the ring's σ_v plane of symmetry. The spectrum also reveals a tunneling splitting with a characteristic 3:1 intensity ratio that arises from a water-centered internal rotation about its C_2 axis which exchanges its hydrogen atoms with an estimated barrier of approximately 2.7 kJ/mol (B2PLYP-D3(BJ)/def2-TZVP). Based on symmetry-adapted perturbation theory (SAPT) calculations, electrostatic and dispersive interactions are shown to be the most stabilizing contributors behind the formation of thiophene–w.